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Photocrosslinking of ferroelectric polymers and its application in three-dimensional memory arrays

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An I-line photolithography process for ferroelectric polymers is developed. It is based on photocrosslinking using a bisazide photoinitiator. Patterned layers were realized down to 1–2 μm resolution. Crosslinking yields a close-to-insoluble ferroelectric polymer network that counter intuitively has similar ferroelectric properties as a noncrosslinked film. The negative process is used to stack ferroelectric films on top of each other to make three-dimensional cross-bar arrays of nonvolatile ferroelectric capacitor memories. © 2011 American Institute of Physics.

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Nonvolatile electronic memories using ferroelectric copolymers of vinylidene fluoride and trifluoroethylene, P(VDF-TrFE), are on the brink of commercialization. First products will be based on ferroelectric capacitors in combination with external conventional read/write electronics. Low-cost manufacturing based on solution processing and better control of the long term reliability parameters are allowing the first passive matrix capacitor arrays to be introduced.¹ In a typical memory array, the capacitors are defined by patterning the top electrode into columns and the bottom electrodes into rows. The memory state from a capacitor is changed by addressing the corresponding row and columns and applying a bias that will provide the desired ferroelectric polarization. To program all memory elements, each row is sequentially addressed. An important advantage is that the information is nonvolatile, i.e., the ferroelectric polarization remains when the power is turned off.

For low density capacitor arrays it may not be needed to pattern the ferroelectric film. In future, however, it may be beneficial to integrate patterned ferroelectric thin films with transistors² or other electronic components on the same substrate, i.e., heterogeneous integration. P(VDF-TrFE) films have been patterned by inkjet printing.^{2,3} Fabrication of complex, integrated circuits requires patterning of uniform P(VDF-TrFE) films over large area with micron sized resolution. This cannot be realized with printing techniques. Hence, we focused on photolithography of spin coated P(VDF-TrFE) films. Within this process P(VDF-TrFE) polymer chains are crosslinked resulting in an insoluble polymer network that is resistant to most solvents and etchants. Besides high resolution large area patterning, crosslinking opens the way to deposit multiple layers of ferroelectric polymers on top of each other. Stacking of ferroelectric capacitors in a three-dimensional (3D) array is a way to densely pack memory elements. It would reduce the number of electrodes per memory elements because the electrodes in

the middle layers of the stack can program memory element directly above and below. Fabricating such multilayer structures is challenging. In the case of inorganic ferroelectrics, high-temperature annealing is usually required in order for a layer to become ferroelectric. The annealing treatment then destroys or alters the characteristics of the previously deposited layer. For soluble materials it is crucial to ensure that previously deposited layers are totally resistant to the solvents used to deposit subsequent layers, to avoid intermixing or even washing away. One solution is to use evaporated VDF oligomers. Horie *et al.*⁴ recently fabricated two vertically stacked VDF capacitors and demonstrated that these films of VDF exhibit similar ferroelectric characteristics as their polymer P(VDF-TrFE) copolymers. Patterning was achieved by shadow masking. Drawback of this method is that VDF deposition requires processing at very low temperatures and high vacuum.

In this letter, we report on a “negative” photolithography process and its application into 3D memory arrays. The lithography is based on photocrosslinking. The nonilluminated parts are removed, thus, yielding a negative process. A bisazide photoinitiator was used as crosslinking agent.^{5,6} Its chemical structure is shown in Fig. 1(a). A solution of P(VDF-TrFE) and the bisazide is spincoated, and the layer is exposed to UV light. The photoinitiator is sensitive to UV light, more specifically 365 nm (I-line) radiation. Photochemical decomposition of azides leads to formation of singlet nitrenes⁷ and, by intersystem crossing, also to triplet nitrenes. Both can react with C–H and C–F bonds, yielding the desired crosslinked polymer network. By optimizing the concentration of photoinitiator, the dose, and the development conditions, we could realize features down to 1–2 μm lines and spacings [Fig. 1(b)]. Moreover, the crosslinked polymer network became fully resistant to typical solvents used for solution processing of P(VDF-TrFE).

To measure the ferroelectric properties of the crosslinked films we made capacitors. First, bottom electrodes were defined in a 30 nm thick Au layer by standard photolithography. Then, a 250–450 nm thick film of P(VDF-TrFE) with 77

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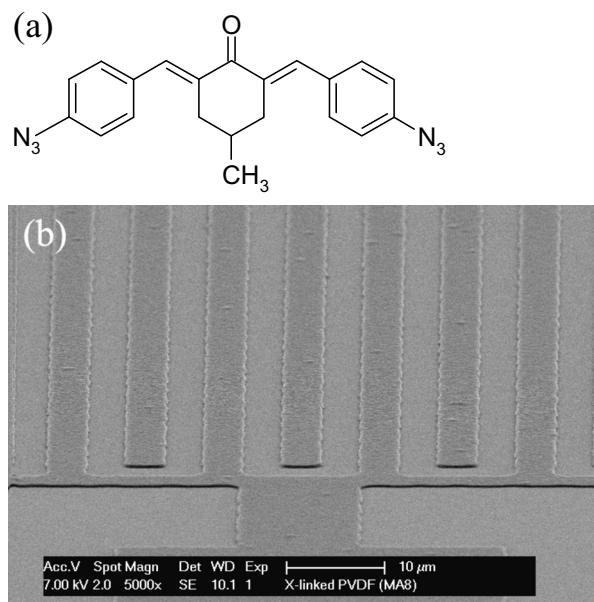


FIG. 1. (a) Chemical structure of the bisazide photocrosslinker and (b) SEM image of crosslinked P(VDF-TrFE) after development.

mol % VDF (provided by Solvay Solexis, Italy) was spin-coated from a 6–8 wt % cyclohexanone solution. To this solution the bisazide was added in a concentration of 2.5–10 wt % relative to the P(VDF-TrFE) content. So, the P(VDF-TrFE):crosslinker ratio was varied between 40:1 and 10:1 by weight. After UV exposure, the layers are developed with methylisobutylketone. This did not result in a significant decrease in layer thickness in the exposed parts indicating that the polymer is sufficiently crosslinked and thus insoluble, even for the lowest P(VDF-TrFE):crosslinker ratio of 40:1. Films were then further annealed at 135 °C for another 1 h to increase the crystallinity of the P(VDF-TrFE) and thereby the ferroelectric response.⁸ Finally, the top electrodes were made by evaporating gold through a shadow mask.

Charge displacement versus voltage (D-V) hysteresis loops were measured at a hysteresis frequency of 100 Hz using a TF Analyzer 2000 from aixACCT. A typical hysteresis loop of a noncrosslinked capacitor with a 400 nm thick noncrosslinked P(VDF-TrFE) film is shown in Fig. 2(a). The saturated loops are symmetric and square with a remnant polarization of + or –70 mC/m². The coercive voltage (V_c), i.e., where D is 0, is found at |32| V, which corresponds to a coercive field (E_c) of approximately 75 MV/m. These results are consistent with literature data.⁹ Also shown in Fig. 2(a) are the loops for crosslinked P(VDF-TrFE) capacitors. The P(VDF-TrFE):crosslinker ratio was varied between 40:1 and 10:1, using a P(VDF-TrFE) concentration of 8 wt % in this case. The hysteresis loops of the 40:1 crosslinked film were indistinguishable from the noncrosslinked capacitor. The ferroelectric properties are well preserved when crosslinking the ferroelectric polymer, a result that is nontrivial if one considers that polarization switching involves field-induced reorientation of the polymer chain and a crosslinked polymer network is usually characterized by restricted chain mobility. For higher crosslink concentrations the remnant polarization decreases and the switching voltage increases. Most likely, at these concentrations the crosslinking density is leading to a higher energy barrier for polymer reorientation, and the ferroelectric properties are therefore impaired. Figure 2(b)

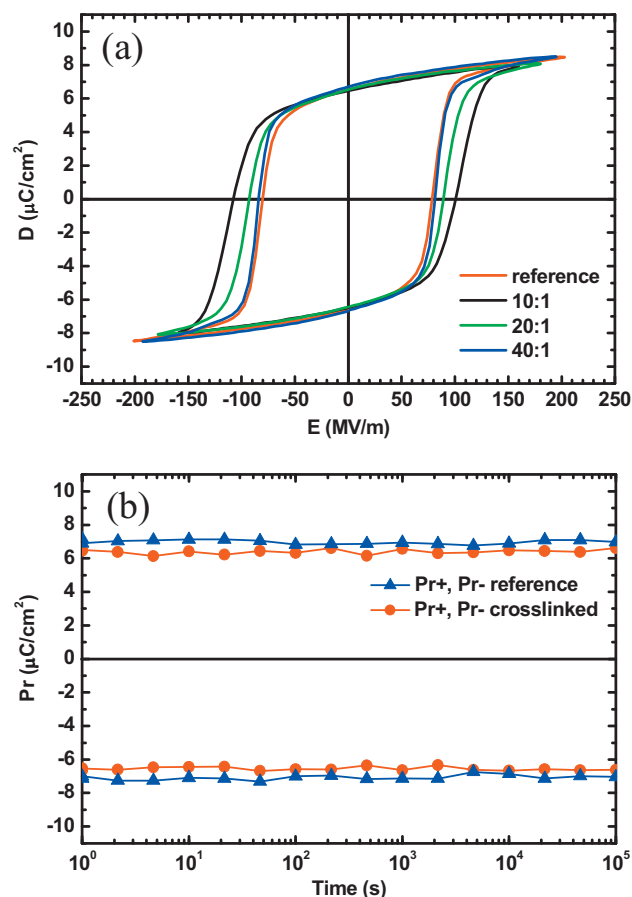


FIG. 2. (Color) (a) D-E loops for a 440 nm thick P(VDF-TrFE) films sandwiched between gold electrodes (device area 0.46 mm²). The P(VDF-TrFE):crosslinker ratio was varied between 10:1 and 40:1. (b) Data retention measurement of a photocrosslinked film of 440 nm thickness after programming by a voltage pulse of 80 V for 10 ms. As a benchmark, the retention properties of a film with no crosslinker that was processed and programmed under identical conditions are shown.

shows the data retention of a capacitor memory using a crosslinked ferroelectric film sensitized with a 40:1 P(VDF-TrFE):crosslinker ratio. As a benchmark, the retention properties of a film with no crosslinker that was processed and programmed under identical conditions are also shown. Data retention was measured by measuring the remnant switching current at a given time after it has been programmed by a voltage pulse of 80 V for 10 ms. those obtained for a reference device. Up to 10⁵ s, the loss of ferroelectric polarization is negligible for both capacitors.

Differential scanning calorimetry measurements are performed on pure P(VDF-TrFE) and cross-linked P(VDF-TrFE) (10 wt % cross-linker), to study the influence of crosslinking on the phase transition behavior of P(VDF-TrFE). The thermogram shows that the Curie transition and the solid/liquid transition occurs at approximately 128 °C and 141 °C, respectively, in both films. Hence, the annealing step that is usually carried out just below the melting temperature to increase the crystallinity of the film, is kept at 135 °C in all samples.

IR measurements are performed on pure P(VDF-TrFE) and cross-linked P(VDF-TrFE) (10 wt % crosslinker), to study the evolution of structural phases upon annealing. The 1288 cm⁻¹ vibrational IR band (A1 symmetric stretching vibration of CF₂) was used to monitor the crystalline ferroelec-

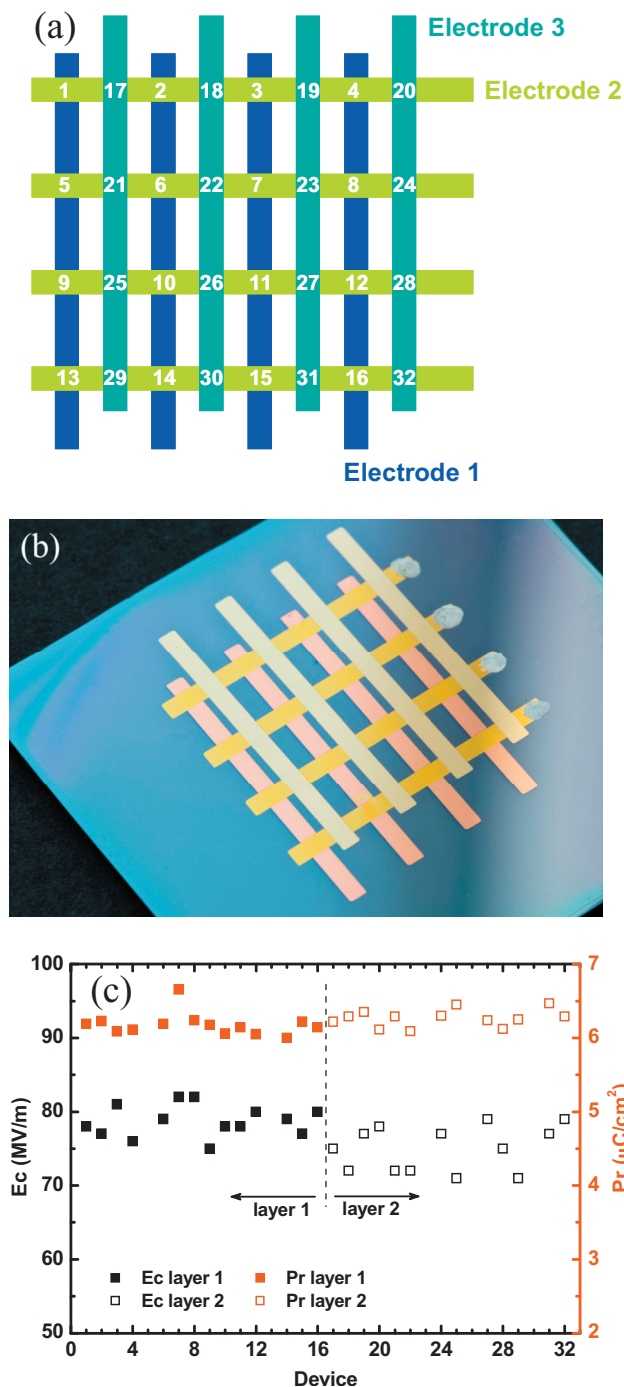


FIG. 3. (Color) Schematic (a) and photograph (b) of $2 \times 4 \times 4$ 3D-array. Electrode width was 1 mm. (c) Impression of the uniformity of coercive field, E_c , and remnant polarization, P_r , of the first and second layer of P(VDF-TrFE) capacitors of the memory array.

tric β -phase in P(VDF-TrFE) films.¹⁰ We found that the ferroelectric β -phase content in the as-cast films is low and approximately the same for the pure film and the P(VDF-TrFE) film containing 10 wt % crosslinker after photoexposure. After subsequent annealing at 135 °C, the A1 band increases in relative intensity, indicating an increased ferroelectric β -phase content for both films. The increase in A1 band was found to be less for the annealed crosslinked film. These IR measurements unambiguously show that crosslinking effectively impairs the crystallization of P(VDF-TrFE) during thermal annealing. The lower ferroelectric β -phase

content in the crosslinked film explains the difference in ferroelectric response at high crosslink concentration [Fig. 2(a)].

We used the photocrosslinking process to deposit multiple ferroelectric layers on top of each other. In each layer the capacitors are integrated in a 4×4 cross-point array. A schematic of an array is shown in Fig. 3(a), and a picture of a finished array [two stacked P(VDF-TrFE) memory layers and three metal layers] is shown in Fig. 3(b). Column and row electrodes of multilayered (3D) nonvolatile memory arrays were made by evaporating gold through a shadow mask. The memory layer was a crosslinked P(VDF-TrFE) film. By applying a bias to the corresponding row and column and grounding all other electrodes the specified memory capacitor can be correctly read and programmed. An impression of the uniformity of the memory characteristics of the $2 \times 4 \times 4$ memory cells in the bottom layer, as extracted from the D-V hysteretic loops, is given in a plot of E_c and P_r per layer [Fig. 3(c)]. The distribution of E_c and P_r of the bottom layer is comparable to that of the upper layer. The average values of E_c and P_r are 77 MV/m and $6.2 \mu\text{C}/\text{cm}^2$ with a standard deviation of 3 MV/m and $0.14 \mu\text{C}/\text{cm}^2$, respectively. Similar values were found for a 4×4 capacitor array using non-crosslinked P(VDF-TrFE), illustrating the proof-of-principle of 3D stacking.

In summary, we show that it is possible to crosslink and pattern P(VDF-TrFE) layers down to micrometer resolution using a bisazide photoinitiator. By crosslinking a polymer network is formed and the layer becomes insoluble, ferroelectric properties are largely retained. The coercive field was constant. The remnant polarization was decreased by approximately 5%–10% compared to pristine layers. This patterning technology is versatile and scalable and has direct applications in the realization of multilayered (3D) nonvolatile memory arrays, and integration of memory transistors with logic thin-film circuitry.

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¹Q2 Interim report Thin Film, <http://www.thinfilm.se/news/38-press-releases/218-q22010>.

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